

Structure and Dynamics in Surfaces of Polymers and Organic Electronic Materials

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Introduction

Surfaces of polymeric materials play increasingly important roles as polymer applications as thin films become more predominant, especially in high-technology devices. In this regard, the structure and dynamics in the top surface layer, ca. 1-2 nm, are of most critical importance, but they are very difficult to determine by conventional experiments employed mainly for bulk samples. In order to investigate the detailed surface characteristics of polymer films, we have performed atomistic molecular dynamics simulations^{1,2} and employed novel experimental methods such as the NEXAFS spectroscopy.^{3,4} The geometric confinement of the surfaces and the necessity to minimize the surface energy lead to the significant molecular organization and orientation at the surfaces, much more pronounced than those in the bulk films.

Results and Discussion

The results from our atomistic molecular dynamics simulations show that the detailed surface structures can not be universally described by a simple model of connected Lennard-Jones spheres, for example. In other words, the surface structure and hence the relevant properties are strongly dependent upon the atomistic details of the repeating monomer structure. This is well illustrated by the results shown below for poly(*n*-butyl methacrylate) and polytetrafluoroethylene.⁵

The density profiles of various poly(alkyl methacrylate)s show a significant variation of the thin film structures as the alkyl side chain is increased from methyl to ethyl and *n*-butyl. For example, as seen in Figure 1, poly(*n*-butyl methacrylate) surfaces exhibit a strong segregation of backbone carbons, with the density of all atoms noticeably higher than that of the bulk. These results, not found at all for polymethylenes,² are less pronounced for poly(methyl methacrylate). It is likely that this surface structure reflects the presence of the layer-like nanostructure proposed for certain poly(alkyl methacrylate)s in bulk amorphous state.⁶

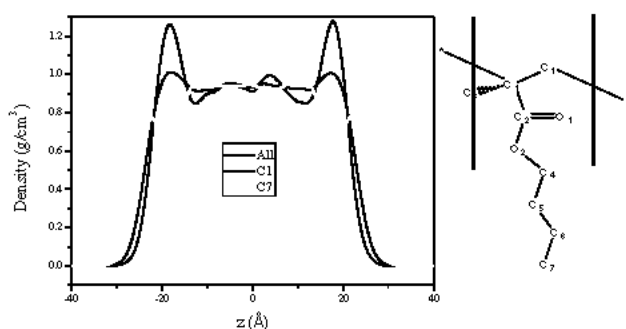


Figure 1. The density profile of poly(*n*-butyl methacrylate) thin films at 450 K. The black lines are for the all atoms, the red line denotes the backbone carbons and the green line is for the terminal methyl of the *n*-butyl ester side groups, with the density profiles of the backbones and the methyl groups normalized to that of all atoms.

Figure 2 shows the density profile and the orientational order parameters in perfluoroalkane thin films. The order parameter is defined by $P(z) = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$ where θ is the angle between the Z -axis normal to the film and the segment vector joining the

midpoints of two consecutive C-C bonds, and Z is the thickness-axis coordinate of the mid-point of the vector with zero located at the film center.

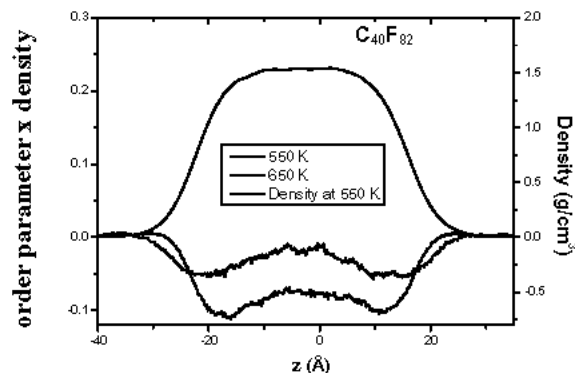


Figure 2. The density profile and the order parameters in *n*-C₄₀F₈₂ thin films. The blue line shows the density profile at 550 K, and the black line denotes the results of order parameter multiplied with density at 550 K and the red line is the corresponding result at 650 K.

For C₄₀F₈₂ films, the density profile is monotonous as is the case for polymethylenes,² but the segment orientation is not randomized as found for polymethylenes and show a strong tendency of the chain segments to orient parallel to the film surface even in the middle of the thin film (ca. 4 nm thickness). Since this order parameter decreases as the temperature increases, this indicates that the relatively stiff conformational properties of perfluoroalkanes are responsible for the presence of this orientation in thin films.

From the experimental studies, we have found that oligomeric electronic materials such as oligofluorenes⁷ are much more readily aligned to from monodomains by employing rubbed polymeric films or by direct rubbing of the free surfaces, as compared with polymers. Moreover, the order parameter in the surface layer of aligned oligofluorene films is much greater than that of the bulk film. The alignment mechanism and the noble anisotropic optoelectronic properties provided by such unique molecular orientations will be discussed.

Acknowledgment

This work was supported by Korea Research foundation (KRF-2001-015-DS0032), Brain Korea 21 Program (Chemistry and Molecular Engineering), and A. v. Humboldt Foundation.

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